In situ trace element analysis of macerals and minerals in coals using laser ablation ICP-MS.

D.A. Spears[1,*], A.G. Borrego[2], A. Cox[1] and R.M. Martinez-Tarazona[2]
[1]Centre for Analytical Sciences, Department of Chemistry, University of Sheffield, Sheffield, UK. [2]Instituto Nacional del Carbon, (CSIC), C/Francisco Pintado Fe No 26, 33011, Oviedo,Spain.
Email: d.a.spears@sheffield.ac.uk

Abstract
Laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) offers the possibility of directly analysing individual, micron-sized coal components down to the ppm level using polished sections or blocks and therefore free from the need to separate components. A number of representative coals have been analysed for V, Ge, Ni, Cu, Zn, Sr and Ba, which were known to have some organic association. Aluminium and Fe were included as controls on the abundances of the clay and pyrite. Sporinite was found to have low trace element concentrations, inertinite higher concentrations of detrital elements and vitrinite higher concentrations of V, Ge and Al. It is thought that these latter elements became concentrated during diagenesis from circulating porewaters.

Keywords: LA ICP-MS, trace elements, coal petrography

Introduction

Trace elements in coals are of current interest because of environmental concerns. Resulting from coal-combustion trace elements are released into the environment and concentrations are increased above the natural background levels. It is not only the trace elements in the atmospheric emissions that are important but also those elements that are mobile during weathering that are associated with the solid combustion residues. If all an element is released into the environment then only absolute concentrations are important. If the release is partial, and this depends on the association within the coal, then the location of an element in the coal is important. In addition, it is only if the location of an element is known with certainty that the geochemistry can be fully appreciated. Information about the geochemistry is clearly of academic interest, but once there is an understanding of location and origin of elements in coals predictions can be made for other coals, thus influencing mining and coal-treatment strategies. It is interesting to note that some of the first materials to be analysed by Goldschmidt in the 1930s (1954) for trace elements were in fact coals, or more precisely coal combustion products. The samples were in a form suitable for analysis by the then new method of optical spectroscopy, which later became the analytical workhorse in the 50s and 60s before the advent XRF and atomic absorption spectroscopy. High concentrations were noted for some elements raising the possibility that coals could be a source of rare elements.

One aim of the current work has been to explore the potential of laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) as an analytical tool for the in situ trace element analysis of minerals and macerals in coals. The laser beam can be focussed down to less than ten microns enabling very small samples to be analysed. The laser vaporises a hemispherical hole in the solid sample and therefore the volume of the sample analysed varies as a power function of the diameter of the beam. The sensitivity at the minimum beam diameter that can be achieved using ICP-MS depends on the element, but detection levels in the low ppm range are readily achievable. A larger beam diameter was used in the current work in order to satisfactorily

analyse a particular suite of trace elements. LA ICP-MS has been used before for the analysis of coals. Lyons et al (1990) used this approach in an examination of macerals in the UK Swallow Wood Coal. Many of the elements were thought to be present in finely dispersed mineral matter, with the possible exception of Al, K, Fe, Ga and Sr in the vitinite and cutinite. Querol and Chenery (1995) used LA ICP-MS to obtain trace element analyses of individual grains in polished blocks of coal. In addition to sulphide minerals, the macerals vitrinite, liptinite and fusinite were also analysed. Booth et al (1999) used LA ICP-MS to scan polished blocks of coals to obtain average analyses to augment conventional XRF analyses for elements such as Hg, Cd and Sb. The detection limits achieved with the LA ICP-MS were in the μg/kg range (ppb). The scanning mode of the LA ICP-MS was also adopted for the analysis of fly ash particles (Spears, 2004). The data were statistically analysed to overcome a problem associated with the small mean grain size of the particles (8 μm). This approach of using the scanning mode and statistically analysing the data was further developed in Spears et al (in press) dealing with selected coals and also in this current paper. Although there have been relatively few papers in which LA-ICP-MS is applied to coals and combustion products the technique and the instrumentation are evolving rapidly, particularly in the fields of environmental and biological analysis.

In petrology the electron microprobe is the most commonly used method to obtain direct, quantitative analyses of in situ minerals, but detection limits are too high (generally about 100 ppm) to analyse many of the trace elements in coals. Indirect methods are usually used to determine the distribution of trace elements in coals and either make use of the natural variation in a suite of coals or create variation from a single coal by chemical or physical fractionation. The latter approach followed by a statistical analysis was used to determine the element distributions in a coal from the Yorkshire-Nottinghamshire Coalfield (Spears and Booth, 2002; Spears, 2002). The statistical analysis is, in essence, an extension of the observation by Goldschmidt (1954) that the Ge organic association in the coal is demonstrated by the inverse relationship between concentration and ash content. Assuming a linear relationship the equation is of the form $y = mx + c$, where the intercept value gives the organic composition. The calculated trace element distributions for organic matter, pyrite and silicates are shown in Table 1. These have provided the impetus to the present work in that although we have the trace element compositions of the major components of the coal, including the organic matter, the role of different macerals is undefined. Using the LA ICP-MS it was hoped to remedy this and also to provide additional information on the minerals.

Methods

Coal samples were prepared as polished thin sections and the petrography recorded across marked transects. These transects were then ablated and the counts for the chosen elements recorded. The element profiles and the petrography were then compared. The distance scanned was of the order of 10mm at a scan speed of 30 μm/s. with a beam diameter of 20 μm. In scanning 10mm the number of analyses produced is just over 300. The laser used was a New Wave UP266 Macro and the ICP-MS an Argilent HP 4500. Further information on the operating conditions is given in Spears et al (in press). The diameter of the laser beam (20 μm) was chosen to achieve the desired sensitivity for the elements of interest. Although greater than the size of the many of the grains, it is possible to determine the trace element concentrations in smaller mineral grains making use of diagnostic major elements. For example, in the case of pyrite this would be the Fe concentration and assuming a composition of FeS_2. A limited number of elements can be analysed at one time and the elements selected were those for which an organic source is thought

to be important based on previous work (Table 1). The elements analysed were V, Ge, Ni, Cu, Zn, Sr and Ba, together with Al and Fe to provide a control on the clay and pyrite contents

Table 1
To show the calculated percentage distribution of trace elements between organic matter, the clay fraction and pyrite in the Eggborough coal. The calculation method was outlined in Spears (2002). The calculated values are from the latter publication as is the bulk composition in the final column (Spears and Martinez-Tarazona, 1993).

	Organic (%)	Clay (%)	Pyrite (%)	Bulk pf (ppm)
V	68	32	0	90
Cr	37	63	0	47
Ni	51	28	21	36
Cu	49	16	36	47
Zn	31	37	31	33
Ga	35	65	0	8
Ge	93	7	0	5
As	9	2	89	27
Se	46	6	48	1.3
Br	100	0	0	41
Rb	0	100	0	28
Sr	40	60	0	45
Y	33	67	0	10
Zr	18	82	0	38
Nb	23	77	0	2.9
Mo	27	5	68	3.2
Sn		100		1
Sb	36	29	35	1.3
Ba	13	87	0	121
La	1	99	0	10
Ce	16	84	0	20
Sm	0	100	0	9.2
Pb	32	19	48	19
Th	0	100	0	3.5

in the coal. Pyrite is the major location for As, Se, Mo, Sb and Pb (Table 1) and these elements were not therefore analysed in this work because the emphasis was on finding the organic composition. Minerals contribute to the Sr and Ba concentrations, but an organic source was also suspected and both elements were included in the scans. Conversion of the count rates for the selected elements into concentrations was achieved using whole coal analyses based on XRF analyses. A number of different samples of the same coal were scanned with the laser to ensure that the results were representative of the whole coal. In previous work (Booth and Spears, 1999), good calibrations were obtained on scans of crushed coal, thereby eliminating any problems of non-homogeneity. However, as the coals used varied in their maceral composition, the good calibrations achieved demonstrated that macerals were not being ablated in a significantly different manner, which was potentially another problem in the present work.

In the previous section we noted that a long-established geochemical approach is based on the

statistical analysis of the variation in a suite of samples. The variation may be natural, or the result of physical or chemical fractionation. The same approach is also possible using the LA ICP-MS by statistically analysing all spot analyses, approximately 300/10mm, in one or more transects.

Coal Samples

The coal chosen for study was one for which information on composition and element distributions were already available (Table 1). This bituminous Pennsylvanian coal from the Yorkshire Coalfield was collected at the Eggborough Power Station and was described in Spears and Martinez-Tarazona (1993). Three separate samples of this coal were prepared as polished thin sections and ablated. The samples were all banded on a scale less than the size of the transects, i.e. there was a significant petrographic variation.

Results and Discussion

A transect of one of the Eggborough samples showing the V counts is shown on Figure 1. The low values at either end of the scan represent the instrumental background. Once the transect begins the V counts are all above background. Of the elements analysed only the Ge counts and to a lesser extent those for Zn are close to background levels. The V counts increase significantly from 100-250 seconds and this corresponds to a vitrinite-rich band in which clean collotelinite bands are present at 150-180 seconds. The average V concentration in these areas is about 60 ppm, which agrees with the

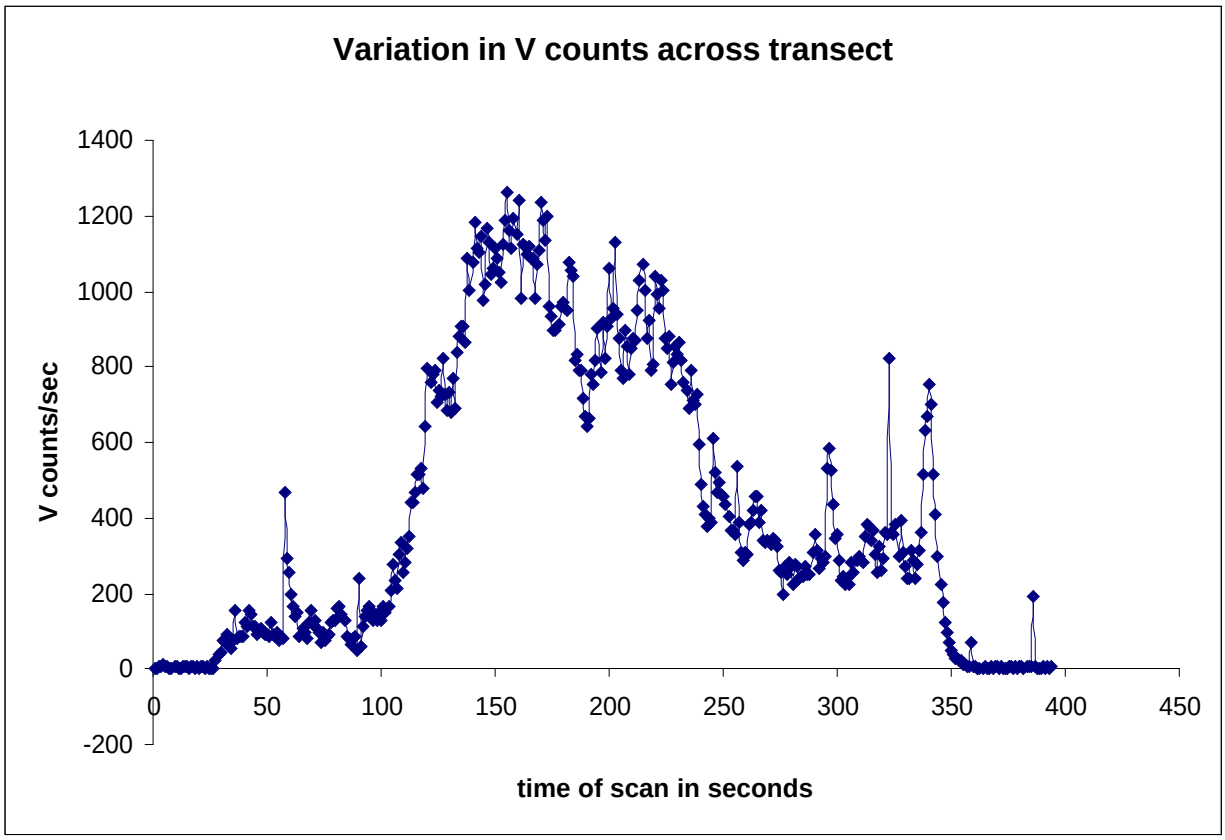

Figure 1. To show the variation in the V counts across a laser ablation ICP-MS transect of Eggborough coal

value shown on Table 1. Sporinite is also present but is not thought to account for the higher V concentrations, because elsewhere higher sporinite contents do not correspond with increased V counts. In fact the laser ablation ICP-MS analyses show that sporinite is particularly low in trace elements, which is consistent with the origin of this maceral as well-preserved exines of resistant material (ICCP, 2001). The natural protection of the spores restricts reaction between the organic matter and ions present in the interstitial waters. In the other sections of this coal V concentrations are again higher in the vitrinite rich areas and collotelinite would appear to be responsible. A similar conclusion was reached in studying a small number of other coals with, in addition, collodetrinite being a major contributor to the V content of the coal.

In the Eggborough coal the concentration of Ge is 5.0 ppm, of which over 90% is thought to be in the organic matter (Table 1). The count profiles for Ge in different transects are similar to V in some but not in all. In some profiles Ge and V do correlate at the 95% confidence level and both are contained in the vitrinite rich areas. In other profiles Ge counts remain uniformly low even for vitrinite rich bands with higher V counts. In other coals examined Ge is comparable with V in that concentrations are higher in the vitrinite areas but in other petrographically similar areas the Ge is low, unlike the V. It would appear that Ge is concentrated in only some of the vitrinite-rich areas. The explanation for this could be that Ge has greater mobility in the diagenetic environment than V. In some sections, where collotelinite is concentrated, Ni, Sr and Ba are also higher. In these transects the relationships between all elements in the group Ni, Sr, Ba, Ge and V are all significant at the 95% confidence level. Calculations (Table 1) show an organic association for this group of elements and the laser work confirms this. Higher trace element concentrations in the vitrinite are understandable because of its reactive nature (ICCP, 2001) and the possibility of capturing elements from solution during diagenesis.

High concentrations of Al and Fe were noted in inertinite-rich (mixture of semifusinite, macrinite and funginite) areas of the scans. This is thought to be due detrital minerals, mainly clay minerals. Clastic material in inertinite is well-documented and its presence is thought to be favoured by the conditions leading to the formation of inertinite, that is periodic dry periods (ICCP, 2001). The only trace elements analysed that are marginally higher in the inertinite are Cu and Zn. However, the elements analysed were those thought to have an important organic association. Trace elements that would be predicted to be concentrated in the inertinite are those on Table 1 with a dominant clay association.

Two elements that have markedly different profiles in the scans to the V are Cu (Figure 2) and Ni. Count rates are much higher over a short section of the scan. The Fe profile is closely comparable and correlation coefficients are highly significant between the elements. Such a profile, ie short duration high intensity peaks, is due to dispersed mineral grains, in this case pyrite. Although smaller than the beam diameter the trace element concentrations can be calculated for the pyrite assuming a composition of FeS_2 . Although Cu and Ni have higher concentrations in the pyrite than other components it is the organic matter that makes the major contribution to the total in the coal (Table 1). Ni does increase by a small amount in the vitrinite rich areas, where the concentration is about 10ppm. The concentration level for Cu is similar but increases associated with specific macerals were not detected. Although the concentration levels for both Cu and Ni are low in the organic matter, the overall contribution of the organic matter to the whole coal is significant.

Although major increases in Al can be attributed to minerals, for example in the intertinite, there is evidence of small increases in Al in the vitrinite areas. This is illustrated on Figure 3 in a plot of Al against V. High Al and low V values are due to the minerals, whereas low Al and high V values are due to the organic matter. However, in the latter group V and Al are related, so that for any V value there is a minimum Al value. The implication is that not only is the V in the organic matter, but so to is some of the Al. The Al could be contained within the organic structure or might

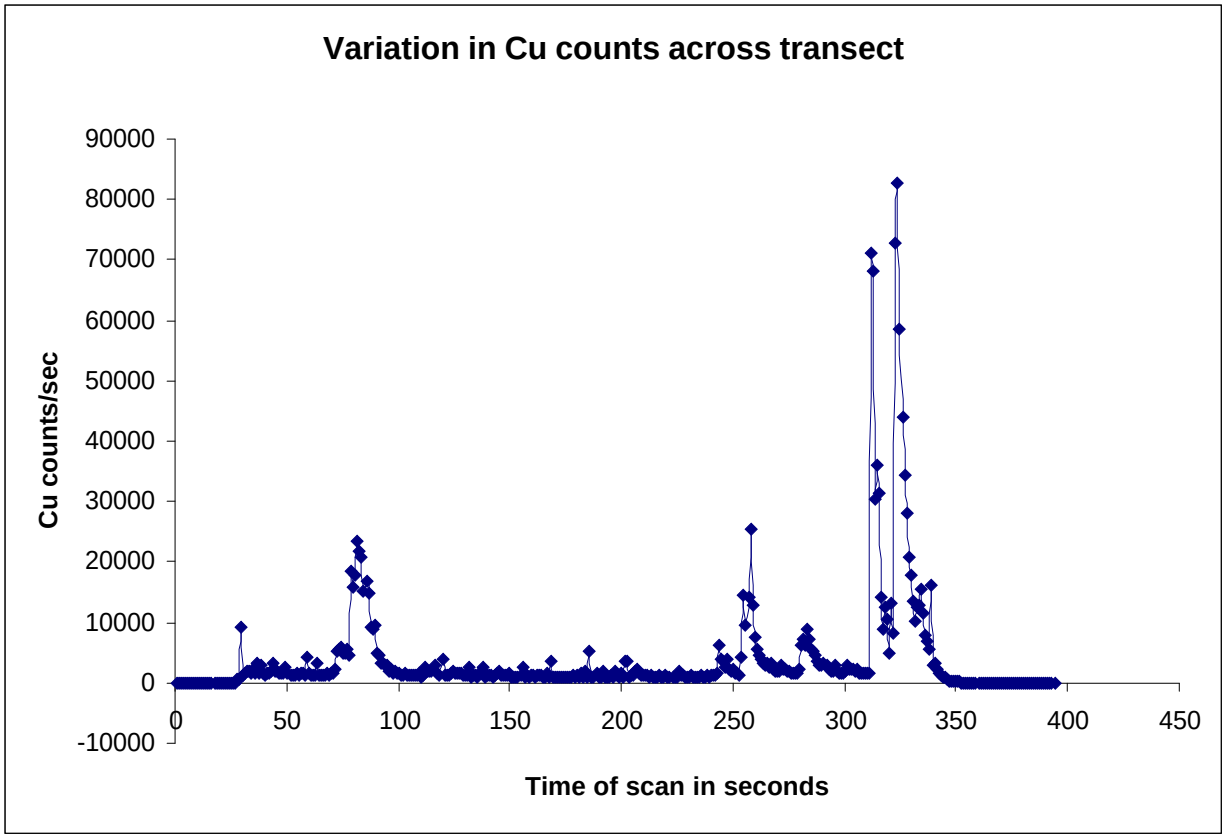

Figure 2. To show the variation in the Cu counts across a laser ablation ICP-MS transect of Eggborough coal

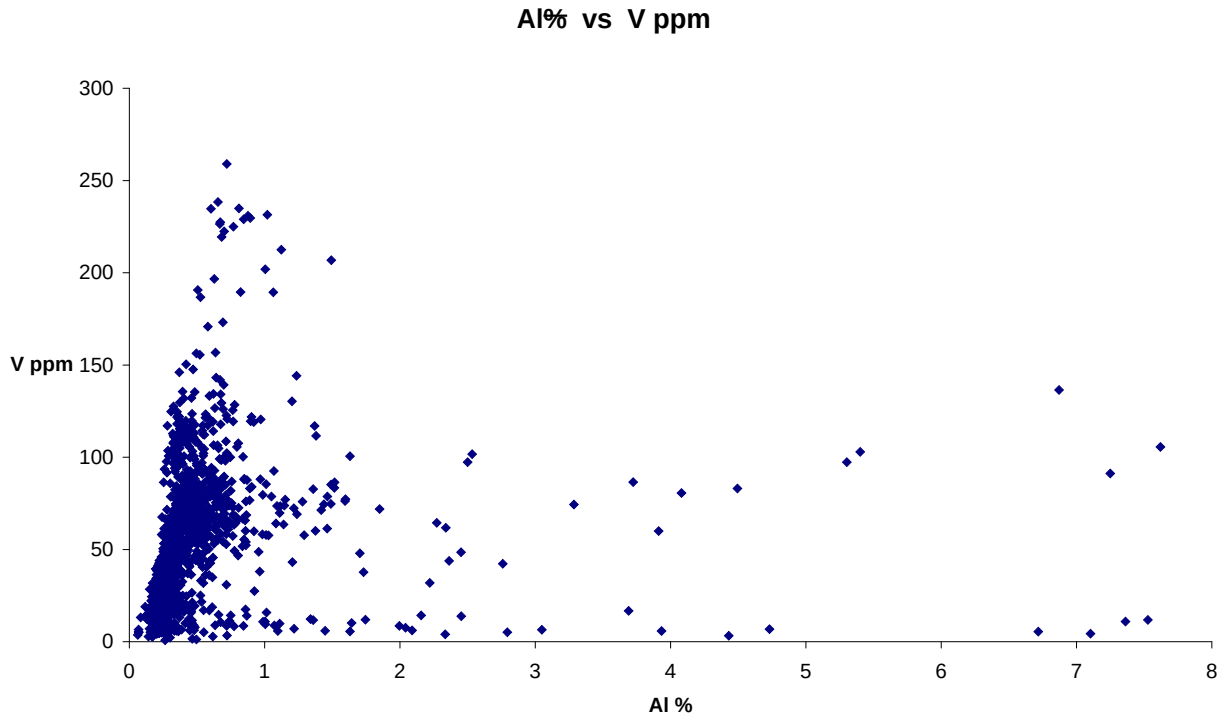

Figure 3. To show the relationships between the Al % and the V ppm concentrations in the Eggborough coal.

be present in finely dispersed clay minerals. Non-mineral, inorganic elements in coals have recently been described by Ward el al. (2007) based on the electron microprobe. One line of evidence for the organic location, also used in the present work, comes from the uniform distribution of elements and the overall consistency in the baseline levels, rather than the spike-like peaks expected from micron-sized mineral inclusions. Vanadium and Ge are known to be mobile during diagenesis (Yudovich, 2003). Aluminium, on the other hand, is relatively immobile. One possibility for the organic association of Al, V and Ge could therefore be that Al originates in the plant material and is retained to a significant degree, whereas Ge and V, similarly sourced, are more mobile and may be lost by leaching or retained by the reactivity of the macerals. Such an explanation envisages redistribution of V and Ge within the peat during coalification. In some samples, Ge does not follow V, which could be due to greater mobility. However, the presence of diagenetic kaolinite infilling cell structures is clear evidence of the mobility of Al within the coal. From this evidence some mobility of Al during diagenesis in the coal can be assumed and the observed higher concentrations of Al, V and Ge in the vitrinite may be a function of the reactivity of the maceral during coalification and its ability to capture all three elements from solution.

Conclusions

- Laser ablation ICP-MS is an extremely useful method for the in situ determination of trace element distributions in coals. The elements analysed were V, Ge, Ni, Cu, Zn, Sr and Ba, all of which were known to have a significant organic association from previous work, and Al and Fe as controls on mineral abundances.

- Using the laser in the scanning mode reveals the non-uniform nature of the coal with sharp peaks associated with minerals such as pyrite, whereas the count rates for the macerals are more uniform.

- In addition to a visual comparison of petrography and element profiles in the scans, a statistical analysis of the data has proved invaluable. Using this approach it is possible to obtain concentration levels for individual components, even though the grain size is significantly less than the diameter of the laser beam.
- Sporinite contains low trace element concentrations; inertinite has higher concentrations of detrital-associated elements, and vitrinite (collotelinite and collodetrinite) higher concentrations of V, Ge and Al.
- It is proposed that V, Ge and Al were concentrated during diagenesis, possibly entirely from redistribution within the coal seam. It is possible, and for Al in particular, that some proportion of that present was residual from the parent material.

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